

Advances in metal halide perovskite ultrathin nanowires

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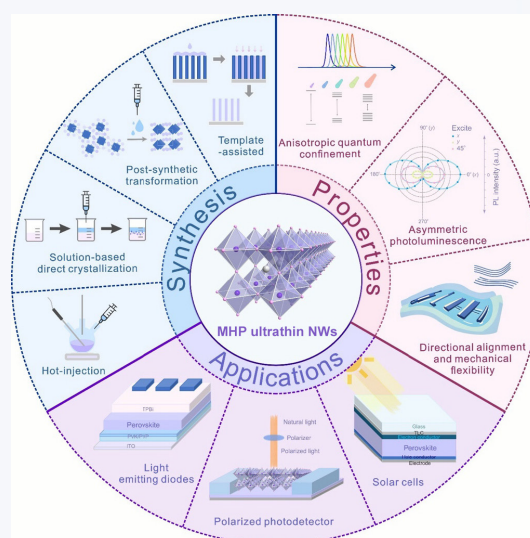
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ABSTRACT: One-dimensional metal halide perovskite (MHP) nanowires (NWs) have recently emerged as highly promising optoelectronic materials due to their high aspect ratio, anisotropic quantum confinement, nonlinear optical response, unique mechanical flexibility, in addition to the well-known advantageous properties inherent to MHPs. In this review, we discuss the recent advancements in the synthesis, characterization, and properties of MHP NWs, particularly with their diameters below the Bohr radius (referred as ultrathin MHP NWs). Key future directions are highlighted, including refining synthesis methods for atomic-level control, understanding the growth mechanisms, improving stability through surface passivation, exploring lead-free alternatives to mitigate toxicity concerns, and achieving novel and unique properties. These advancements will enable ultrathin MHP NWs to play a pivotal role in advanced applications in various optical, optoelectronic, and photonic technologies.

KEYWORDS: metal halide perovskites, ultrathin nanowires, anisotropic quantum confinement, synthesis, optical and optoelectronic properties



1 Introduction

Metal halide perovskite (MHP) nanocrystals (NCs) with a general formula of ABX_3 (A: monovalent cation; B: divalent metal cation; X: halide anion) have gained significant interest in recent years due to their unique crystal structure, ionic bonding nature, high defect tolerance, and exceptional optoelectronic properties [1–4]. These materials exhibit near-unity photoluminescence quantum yields (PLQYs), tunable bandgaps, and strong light absorption over a broad spectral range [5–8]. Moreover, their facile and low-cost synthesis, coupled with their high PL efficiency and sharp emission lines, make MHP NCs ideal candidates for various applications such as solar cells, light-emitting diodes (LEDs), lasers, photodetectors, and photocatalysts, [9–16] etc. The tunability of their optical properties by altering composition, and size, along with their capability to form diverse morphologies of nanostructures including zero-dimensional (0D) quantum dots (QDs), one-

dimensional (1D) nanorods (NRs) and nanowires (NWs), and two-dimensional (2D) nanoplatelets (NPLs) and nanosheets, further import their versatility for implementation and integration into the above-mentioned applications [1, 17–24].

Among these different morphologies of MHP NCs, 1D NWs have garnered special attention due to their high aspect ratios and anisotropic quantum confinement, leading to distinct and unique electronic and optical properties [25–29]. In particular, when the thickness of these NWs is reduced below the Bohr diameter of the material, referred as ultrathin perovskite NWs or quantum wires (QWs), their optical and optoelectronic characteristics become highly tunable due to the presence of strong quantum confinement along their short radial dimensions [30–32]. In this case, the reduced dimensionality in ultrathin perovskite NWs enhances charge separation and transport along the long axial direction, while maintaining strong quantum confinement in the short radial direction [33–35]. This combination results in efficient anisotropic charge transport, which is advantageous for applications such as field-effect transistors, LEDs, and photodetectors [36–41]. Moreover, the high surface-to-volume ratio, high flexibility, and mechanical strength of ultrathin NWs makes them an excellent candidate for applications in sensors and catalysis, where largely exposed NW surfaces play a critical role [42–46].

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While much progress has been made in the synthesis and modifications of 0D MHP NCs, controlling the diameter and uniformity of ultrathin NWs still remains a significant challenge. Traditional approaches, such as hot-injection and solvent-mediated reprecipitation methods, have been used to synthesize MHP NWs [30, 47, 48], but achieving uniform and controllable ultrathin diameters with high aspect ratios is still difficult. Furthermore, the stability of ultrathin perovskite NWs, especially under environmental stress (e.g., moisture, oxygen, and light exposure), remains a significant concern [48, 49], posing a major limitation for the practical implementation of such materials in real-world applications.

This review aims to provide a timely overview of the progress made in the synthesis, characterization, and applications of ultrathin perovskite NWs. Herein, we discuss the various methods applied to produce these structures, and highlight the critical challenges in achieving controlled nucleation and growth of ultrathin NWs with high morphological anisotropy. Additionally, we summarize the physical and chemical properties of ultrathin MHP NWs, with a focus on their optical behavior, structural stability, and potential for integration into advanced devices. Finally, we outline some key areas for future research, emphasizing the need for improved stability and tunability of these promising materials to fully realize their potential in optical, optoelectronic, photonic and many other applications.

2 Synthesis of ultrathin MHP NWs

2.1 Hot-injection method

In 2015, Protesescu et al. reported a reliable colloidal synthesis approach to firstly synthesize colloidal MHP particles in nanoscale with tunable sizes [31]. The synthetic approach is based on an injection process of preprepared A-site monovalent cation-carboxylic acid complex (such as Cs-oleate) into a mixture of B-site

metal salt and organic ligands. MHP NCs start to grow instantly after the injection occurs at elevated temperature and stop growing by rapid temperature cooling using an ice-water bath. In 2016, Manna group modified the synthesis by replacing oleic acid with octanoic acid or hexanoic acid with shorter carbon chains, and decreasing the reaction temperature to below 70 °C [47]. They successfully prepared ultrathin CsPbBr₃ NWs with tunable thickness (NW diameter of 2.8, 3.4, 4.1, and 5.1 nm) by varying the concentration of the involved short acid over that of alkyl amines as shown in Figs. 1(a)–1(c). However, both the absorption and PL spectra of these NWs exhibited a lower energy shoulder/tail at ~500 nm indicating partial NW aggregation (Fig. 1(b)), revealing the instable nature of the produced ultrathin NWs. Differently, Yang group applied a hot injection method with typical long chain ligands (i.e., 1-dodecylamine, oleylamine, oleic acid) and a high reaction temperature (160 °C) to synthesize ultrathin CsPbBr₃ NWs along with other side products [30]. They further applied stepwise purifications to improve the NW purity, where ethyl acetate (EA) was used as the anti-solvent (Figs. 1(d)–1(f)). In each round of purification, the supernatant solution was collected and the precipitate was discarded after centrifugation. After three rounds of purifications, they obtained a relatively pure ultrathin CsPbBr₃ NWs (> 70% purity). However, the resulting ultrathin CsPbBr₃ NWs possessed a large amount of surface defects and thus a low emission efficiency due to significant ligand loss caused by the repeated purification processes using anti-solvent [7, 30].

2.2 Solution-based direct crystallization method

The ease of fabrication and processing at low temperatures is one of the most attractive features of MHPs, which not only reduces the fabrication costs and simplifies manufacturing processes, but also opens up new possibilities for large-area, flexible electronics [50–52]. The ligand-assisted reprecipitation (LARP) approach, typically carried out at room temperature (RT), has therefore attracted significant attention [53–55]. In this method, A- and B-

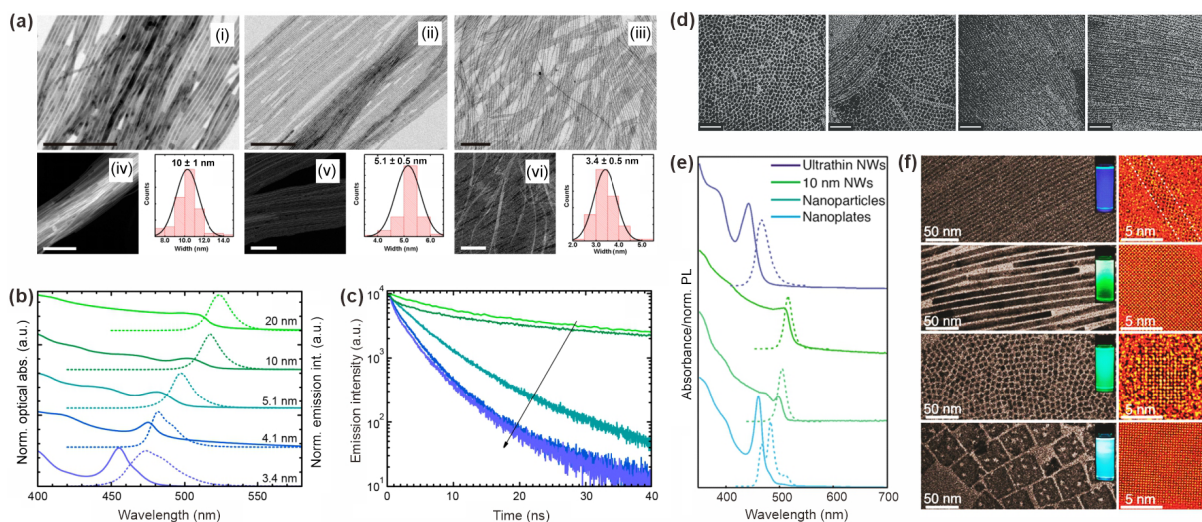


Figure 1 (a) Representative bright field transmission electron microscopy (BF-TEM) and high-angle angular dark field scanning TEM (HAADF-STEM) images of CsPbBr₃ NWs with varying thicknesses: (i) and (iv) 10 nm, (ii) and (v) 5.1 nm, and (iii) and (vi) 3.4 nm. Scale bars represent 200 nm. Corresponding size distributions are shown. Short chain carboxylic acid to alkyl amine ratios are (i) and (iv) 0, (ii) and (v) 0.1, and (iii) and (vi) 0.3, respectively. (b) Optical absorption (solid line) and PL spectra (dashed line) for CsPbBr₃ NWs with different thicknesses. (c) Time-resolved PL decay profiles of CsPbBr₃ NWs excited at 405 nm, with an arrow indicating a thickness decrease from 20 to 3.4 nm. Reproduced with permission from Ref. [47], © American Chemical Society 2016. (d) TEM images illustrating stepwise purifications to obtain ultrathin CsPbBr₃ NWs, with scale bars of 50 nm. The ratio of EA to supernatant increases progressively from left to right. (e) Optical absorption (solid line) and PL spectra (dashed line) of CsPbBr₃ samples, ultrathin NWs, 10 nm thick NWs, nanoparticles and NPLs. (f) Corresponding transmission electron microscopy (TEM) and aberration-corrected high-resolution TEM (AC-HRTEM) images. Reproduced with permission from Ref. [30], © American Chemical Society 2016.

site cation salts are firstly dissolved in a good solvent, such as N,N-dimethylformamide (DMF) or dimethylsulfoxide (DMSO), along with ligands (e.g., oleylamine, oleic acid). Then, the resulting precursor solution is mixed with a poor solvent, such as toluene or hexane, to decrease the precursor solubility and trigger MHP crystallization to form NCs. In 2017, Amgar et al. employed this LARP technique to obtain ultrathin CsPbX_3 ($X = \text{Cl}, \text{Br}, \text{I}$) NWs [56]. The reaction was performed by adding hot Cs-oleate solution to a vial filled with oleic acid and oleylamine serving as organic ligands, followed by the addition of a PbBr_2 precursor solution in DMF. After 10 s of reaction, acetone was swiftly added as the antisolvent to trigger NW crystallization. In addition, different amounts of hydrohalic acids (HX, $X = \text{Cl}, \text{Br}, \text{I}$) from 0–10 μL were introduced into the reaction system to tune the optical features through halide exchange reactions (Fig. 2(a)) [56]. The authors found that the length of obtained NWs was significantly shortened by increasing the added amount of HX acid, which was attributed to that the positively charged oleylammonia (i.e., protonated oleylamine) can perform similarly as Cs^+ cations to block the growth of MHP into long NWs [57, 58]. Unfortunately, the halide composition of obtained CsPbX_3 NWs was not homogeneous as reflected by the multiple emission peaks emerged in their PL spectra, indicating incomplete halide exchange. Around the same time, Kostopoulou et al. also applied the LARP method to synthesize CsPbBr_3 NWs and used anhydrous toluene to quench the reaction, resulting in a mixture of nonuniform NWs and NPLs [59]. The reaction solution was then kept under ambient conditions for one day without stirring. The NPLs were precipitated out of the solution while ultrathin CsPbBr_3 NWs were gradually formed in the supernatant. After one week, however, the NW thickness progressively increased from 2.6 to 6.1 nm with a broader thickness

distribution [59]. In 2019, while utilizing the LARP method to synthesize ultrathin NWs, Peng group added acetonitrile (ACN) into toluene with different proportions to act together as the antisolvent [60]. The synthesized MHP NCs exhibited a morphological transition from nanocubes (with no added ACN) to NWs (with toluene/ACN = 90:10) and further to NW bundles (with toluene/ACN = 80:20) (Fig. 2(b)). Further increasing the ACN amount led to broader and weaker absorption peaks together with the formation of large perovskite crystals that precipitated out of the reaction solution [60]. The authors attributed the results to the addition of the polar solvent ACN, which promoted oleylamine protonation and acted as a Lewis base, forming dative $\text{N} \rightarrow \text{Pb}$ bonds on the NW surfaces, thereby restricting isotropic growth of CsPbBr_3 (Fig. 2(c)) [61]. However, they did not conduct further research to identify the specific facets where growth was inhibited. In 2022, Hu et al. applied a modified LARP method to synthesize ultrathin CsPbI_3 perovskite NWs (Figs. 2(d)–2(g)) [62]. Instead of traditional polar solvents (DMF, DMSO), they used a low-polar organic medium (toluene) to dissolve precursor-ligand complexes (Cs -oleate, PbI_2 -oleylamine). Different from the red emission (peaked at ~ 700 nm) from CsPbI_3 NCs, they obtained ultrathin CsPbI_3 NWs with single-halide component, which presented a blue-shifted emission peaked at 599 nm. A further blue-shifted yellow emission (at 558 nm) with a record high PLQY of 94% was obtained by adding ZnI_2 precursor into the reaction system [62].

In addition, Huang and his co-workers reported another room-temperature colloidal synthesis of ultrathin CsPbBr_3 NWs in 2017 [63]. In their reaction system, the precursor solutions were stirred continuously under RT, followed by direct centrifugation. They further applied a post-synthetic heat treatment process (at 120 $^\circ\text{C}$ for 2 min) to the as-synthesized NWs, which enhanced the PLQY

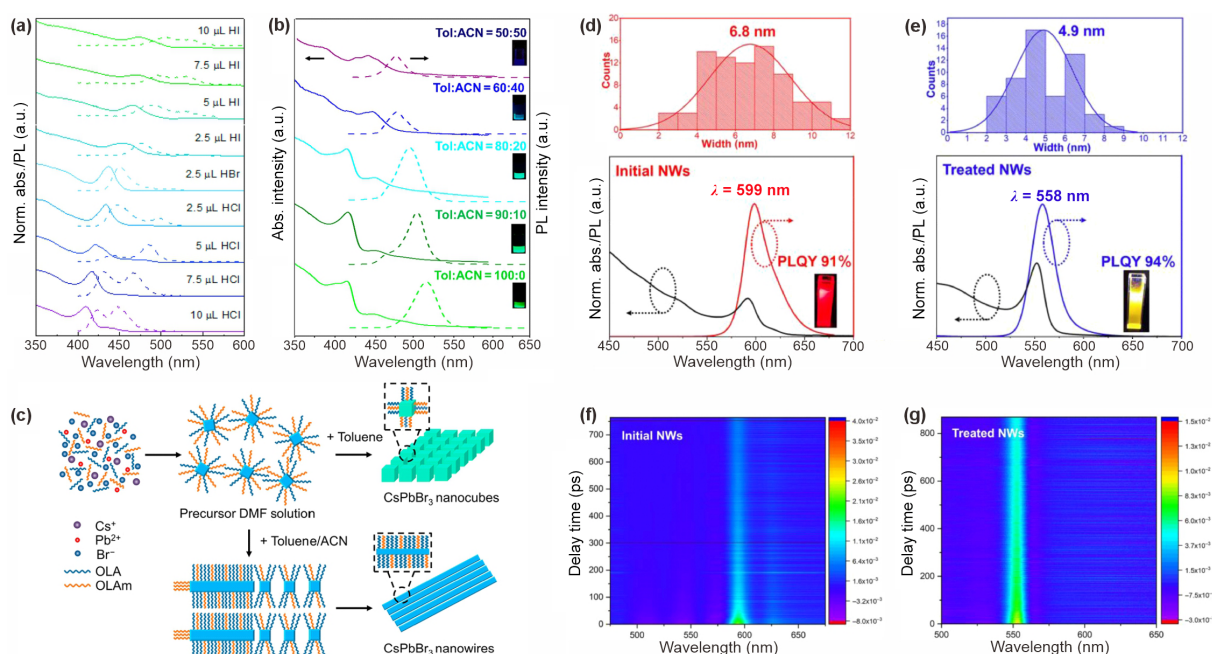


Figure 2 (a) Optical absorption (solid line) and PL spectra (dashed line) of CsPbX_3 NWs synthesized with varying amounts of HI, HBr, and HCl. Reproduced with permission from Ref. [56], © American Chemical Society 2017. (b) Optical absorption (solid line) and PL spectra (dashed line) of CsPbBr_3 NCs synthesized at different volume ratios of toluene/ACN. (c) Schematic diagram illustrating the formation processes of CsPbBr_3 nanocubes in toluene and ultrathin NWs in toluene/ACN. Reproduced with permission from Ref. [60], © American Chemical Society 2019. (d) Thickness distribution (top) and corresponding absorption and PL spectra (bottom) of ZnI_2 -treated ultrathin CsPbI_3 NWs. (e) Thickness distribution (top) and corresponding absorption and PL spectra (bottom) of ZnI_2 -treated ultrathin CsPbI_3 NWs. Pseudo-color femtosecond transient absorption (TA) measurements for the ultrathin CsPbI_3 NWs before (f) and after (g) ZnI_2 treatment. Reproduced with permission from Ref. [62], © Elsevier Ltd. 2022.

of the NWs from less than 1% to over 20% [63]. This process was accompanied by red-shifted absorption and PL peaks, indicating an increase of NW thickness.

2.3 Post-synthetic transformations

Post-synthetic chemical and/or particle shape transformations have been widely employed in MHP NCs to enhance their compositional and morphological tunability [5, 64–66]. This versatile approach enables precise modifications of pre-synthesized NCs, offering access to a broader range of colloidal nanostructures that may be challenging or even impossible to achieve through direct synthesis [67, 68]. Taking advantage of this post-synthetic transformation approach, researchers can fine-tune the properties of NCs, such as their optical and electronic behavior, and gain valuable insights into the mechanisms underlying their growth [69–72].

In 2018, Li et al. applied a thiourea-assisted post-synthetic treatment to convert CsPbBr_3 nanocubes into ultrathin CsPbBr_3 NWs [73]. A thiourea aqueous solution was directly introduced into the crude organic solution of CsPbBr_3 nanocubes to extract Pb^{2+} cations by forming stable Pb^{2+} -thiourea complexes. Under mild heating at 35 °C, the CsPbBr_3 nanocubes firstly transformed into Cs_4PbBr_6 NCs with a zero-dimensional perovskite structure (Fig. 3(a)). And CsBr was subsequently removed by water due to its high water solubility, further transforming Cs_4PbBr_6 into small CsPbBr_3 NCs, which evolve into ultrathin CsPbBr_3 NWs [73]. The resulting NWs showed good colloidal stability and a high PLQY of 60%, albeit with a PL shoulder peak at around 500 nm attributed to

nanocube impurities. The high PLQY was explained by the PbBr_2 rich surface of the obtained ultrathin CsPbBr_3 NWs evidenced by X-ray photoelectron spectroscopy (XPS) measurements [73, 74].

In 2021, Chen group reported a synthesis of ultrathin CsPbBr_3 NWs via a post-synthetic transformation process starting from 0D Cs_4PbBr_6 perovskite NCs, using short alkyl chain organic ligands (Figs. 3(b) and 3(c)) [75]. In the transformation reaction, PbBr_2 precursor together with different organic ligands (i.e., oleic acid, hexanoic acid and octylamine) were added under mild heating condition at 50 °C. After two hours, ultrathin CsPbBr_3 NWs were produced with high purity. Mechanism studies showed that the PbBr_2 -ligand intermediates, which exhibited lamellar structures, served as anisotropic templates directing the growth of CsPbBr_3 NWs [75]. Consistent with the proposed NW growth mechanism, the authors showed that the PbBr_2 -ligand intermediates with larger d -spacings tended to produce CsPbBr_3 nanocubes, while intermediates with smaller d -spacings favored the formation of ultrathin NWs [75].

Besides synthesizing ultrathin CsPbBr_3 NWs through post-synthetic transformation processes, post-synthetic halide exchange reactions were commonly used to produce ultrathin CsPbX_3 NWs containing Cl^- or I^- ions by introducing HX or MX_2 ($\text{M} = \text{Pb}$ or Zn , $\text{X} = \text{Cl}$ or I) precursors to the pre-synthesized CsPbBr_3 NWs solution [30, 56, 60]. In these cases, continuous blue-shifted and red-shifted emission peaks can be observed in Br-to-Cl and Br-to-I anion-exchange reactions, respectively (Fig. 3(d)), demonstrating higher emission tunability by successful inclusion of Cl^- and I^- component to the ultrathin CsPbX_3 NWs.

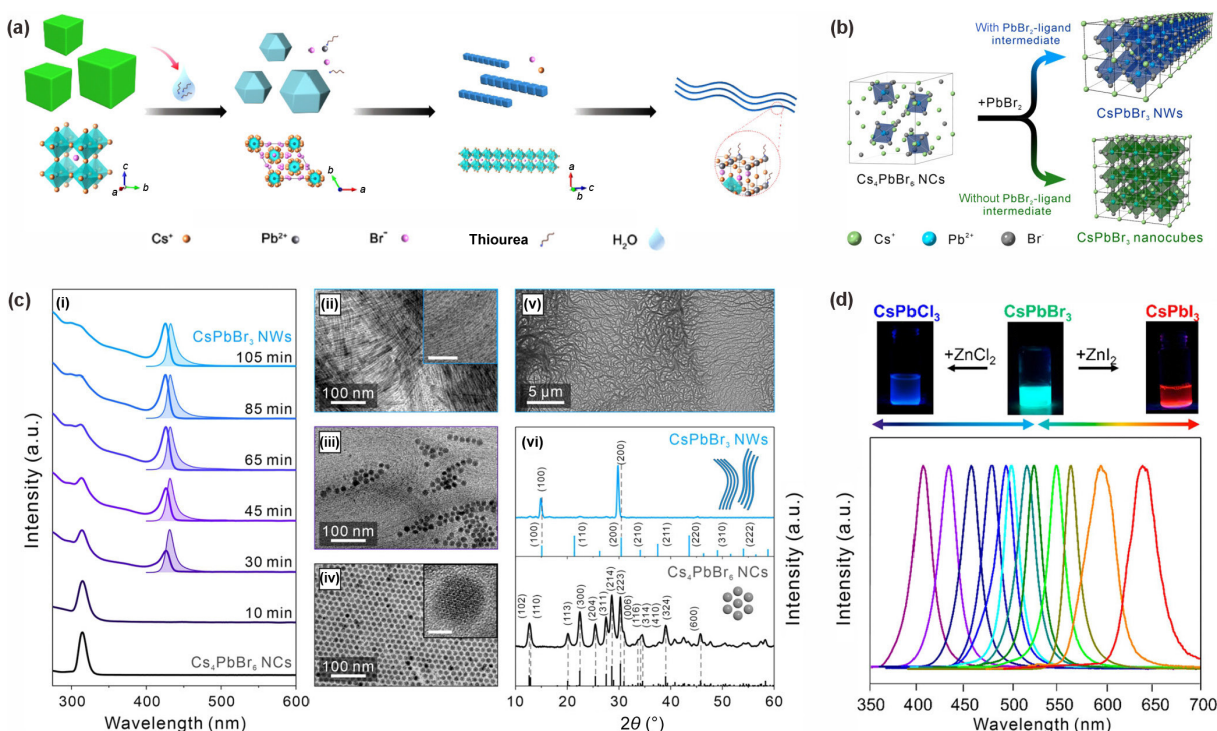


Figure 3 (a) Schematic illustration of the evolution from CsPbBr_3 nanocubes to ultrathin NWs induced by post-synthetic addition of thiourea aqueous solution. Reproduced with permission from Ref. [73], © American Chemical Society 2018. (b) Schematic diagram illustrating the conversion from 0D Cs_4PbBr_6 perovskite NCs to either ultrathin CsPbBr_3 NWs or CsPbBr_3 nanocubes through selective reaction pathways. (c) Evolution of structure, morphology, and optical properties during the reaction illustrated by: (i) optical absorption and PL spectra depicting the transition from Cs_4PbBr_6 NCs to ultrathin CsPbBr_3 NWs over time; Corresponding TEM images showing the evolution from (iv) Cs_4PbBr_6 NCs to (iii) a mixture of Cs_4PbBr_6 NCs and newly formed CsPbBr_3 NWs, and then (ii) ultrathin CsPbBr_3 NWs; (v) Low-magnification TEM image of NW bundles; (vi) X-ray diffraction (XRD) patterns of starting material and final product. Reproduced with permission from Ref. [75], © American Chemical Society 2021. (d) Photographs of ultrathin CsPbX_3 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) NW solutions produced via anion exchange (top) and their respective normalized PL spectra (bottom). Reproduced with permission from Ref. [60], © American Chemical Society 2019.

2.4 Template-assisted method

Template-based space-confined growth method has garnered significant attention as an effective strategy for fabricating NWs with high crystallinity and precisely controlled thickness [76–78]. By utilizing templates with desired nanoscale channels, researchers can precisely control the NC growth process, leading to uniform and high-quality nanostructures [79–81]. This method enables the formation of NWs with precisely defined dimensions, resulting in ligand-free MHP NWs that typically exhibit superior structural and property stabilities compared to colloiddally synthesized MHP NWs [82, 83].

In 2016, the Kovalenko group utilized mesoporous silica (meso-SiO₂) matrices as templates to synthesize elongated perovskite NCs with sizes falling within the strongly quantum-confined regime [84]. High-concentration CsX and PbX₂ precursor salt solutions were infiltrated into the pores of meso-SiO₂ templates, which featured hexagonally ordered 1D channels with varying pore diameters (2.5–7 nm), followed by vacuum drying. The resulting ultrathin, elongated MHP NCs, confined within the meso-SiO₂ matrix, exhibited an ordered mesoporous structure composed of 1D channels resembling NW structures. The bright emissions of these template-synthesized NCs could be finely tuned by pore-size-dependent quantum size effects as well as chemical compositions [84]. In 2019, Zhang et al. developed a self-assembled templating process to fabricate ultrathin CsPbBr₃ NWs [85]. Confined nanochannels were formed by well aligned polymethyl methacrylate (PMMA) fibers through an electrospinning process as shown in Fig. 4(a). These nanochannels acted as templates for the formation of NWs from the infiltrated precursor solutions [85]. After the solvent (DMF) evaporated, ultrathin CsPbBr₃ NWs with a diameter of ~ 2 nm were obtained within the electrospun PMMA fibers. In addition, CsPbBr₃ nanobelts and nanocubes can also be produced by extending the stirring time of the initial DMF precursor solution (Figs. 4(b)–4(e)). In 2022, Fan group used nanoporous anodic aluminum oxide (AAO) as templates to fabricate ultrathin CsPbBr₃ NWs [86]. AAO templates with an initial pore diameter size of around 6.6 nm, were fabricated through an anodic anodization process at a low voltage. Subsequent Al₂O₃

coating via atomic layer deposition (ALD) reduced the pore size from ~ 6 to 2.8 nm (Fig. 4(f)) [86]. Using this AAO template, ultrathin CsPbBr₃ NWs were fabricated by filling the nanopores through a low-pressure closed space sublimation process. More recently, Yang group in 2023 developed a system that utilized single-walled carbon nanotubes (with a diameter of 1.2–1.4 nm) as templates to produce single-unit-cell thick Cs-Pb-I NWs, which can be suspended on monolayer graphene TEM grids [87]. Due to the stability of graphene and carbon nanotubes against heat and polar solvents, they were able to remove the perovskite crystals formed outside the templates using polar solvents and prevent carbon contaminations by annealing at high temperatures [87]. This approach enabled direct *in situ* observation of atomic activities inside the MHP framework, which had only been accessible through theoretical calculations prior to the work [88, 89].

2.5 Solvothermal method

Solvothermal method has also been employed for the synthesis of perovskite NWs with high crystallinity and morphological uniformity [90–93]. This technique involves dissolving precursor materials in a solvent at elevated temperatures and pressures, creating an environment conducive to controlled crystal growth [94–96]. In 2017, Chen et al. applied this method to successfully obtain ultrathin CsPbBr₃ NWs with a morphological purity [91]. Specifically, the synthesis of ultrathin NWs was realized by pre-dissolving the Cs and Pb precursors with ligands (i.e., oleic acid and oleylamine) inside a glovebox and then transferred into the autoclave. The reaction was carried out at 160 °C and the resultant CsPbBr₃ NWs exhibited a thin diameter of 2.6 nm with an absorption peak at 445 nm [91].

3 Current understanding of formation mechanisms for ultrathin MHP NWs

MHP NCs possess highly ionic nature with relatively low formation energies, which leads to rapid nucleation and growth kinetics typically within a timescale of sub-second to a few seconds [97, 98]. This makes *in situ* monitoring of the nucleation and growth events

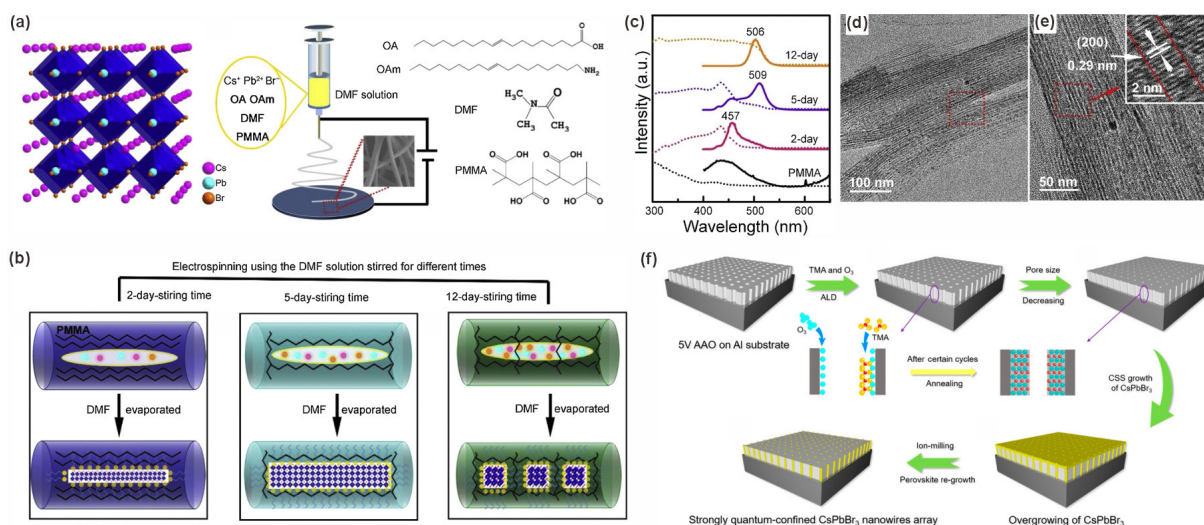


Figure 4 (a) Schematic illustration of the setup for fabrication of ultrathin CsPbBr₃ NWs by electrospinning. (b) Synthesis of CsPbBr₃ nanostructures within the self-assembled nanoscale templates of electrospun PMMA fibers using the DMF solutions stirred for different times. (c) Optical absorption (dashed line) and PL spectra (solid line) of CsPbBr₃ products prepared. (d) and (e) TEM images of ultrathin CsPbBr₃ NWs after removing PMMA. Reproduced with permission from Ref. [85], © Elsevier Ltd. 2019. (f) Schematic process flow of the AAO template-assisted synthesis of ultrathin CsPbBr₃ NWs array. Reproduced with permission from Ref. [86], © American Chemical Society 2022.

to understand the formation mechanism of ultrathin MHP NWs quite challenging [97, 99]. Despite this challenge, researchers have made some important progresses in uncovering key factors that influence the synthesis of ultrathin MHP NWs to help understand their formation mechanisms.

3.1 Seed-mediated growth

Chen et al. discovered that pre-dissolving the precursors was crucial for successful preparations of MHP NWs, otherwise, MHP nanocubes would form instead [91]. They employed a seed-mediated growth mechanism to explain this phenomenon (Fig. 5(a)). When the Cs and Pb precursors are directly heated without pre-dissolution, the gradual dissolving process limits the concentration of effective monomers in solution at any given reaction stage. Consequently, a relatively low number of small nuclei seeds formed in solution, which then grow into nanocubes, a

morphology driven by thermodynamic stability with a limited monomer supply rate during the course of the particle formation reaction [91]. In contrast, when the precursors are pre-dissolved, a high concentration of active monomer ions becomes instantly available upon mixing the Cs and Pb precursors, leading to the rapid formation of a large number of small nuclei seeds [91]. Under this condition, ultrathin NWs merge through a seed-mediated anisotropic growth process caused by assembly and orientate attachment of the initial seed nuclei, yielding MHP NWs with enlarged aspect ratios [91, 100].

3.2 Oriented attachment

Besides the ripening process described by the LaMer growth model [101], oriented attachment has emerged as another key mechanism for NW growth [102–104]. In this process, smaller NCs align and fuse along specific crystallographic orientations to form larger

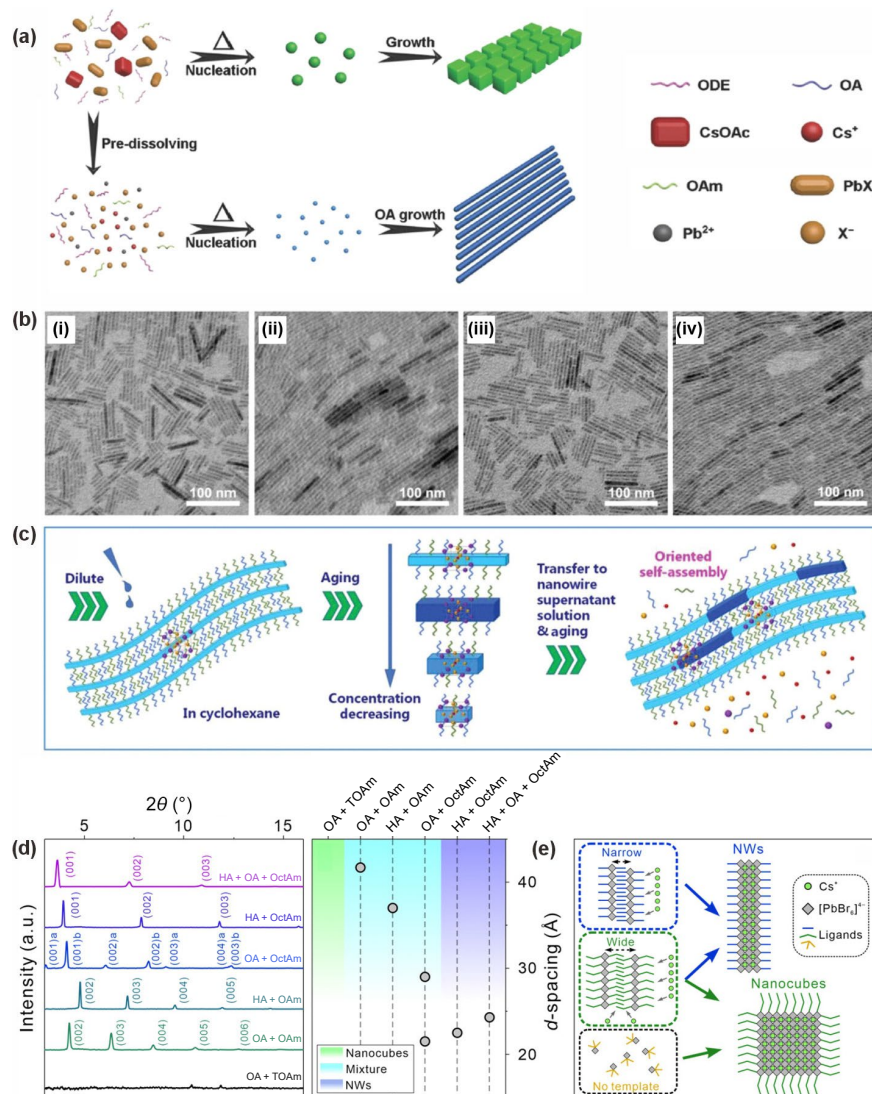


Figure 5 (a) The proposed seed-mediated growth process of CsPbBr₃ nanocubes and ultrathin NWs formation without and with precursor predissolving. Reproduced with permission from Ref. [91], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2017. (b) TEM/HRTEM images of CsPbBr₃ ultrathin NRs and NWs: (i) and (iii) the NRs formed by dispersing NWs in cyclohexane with increasing concentrations, (ii) and (iv) the NWs formed by aging from NRs. (c) Schematic illustration of the transformations between CsPbBr₃ NRs and NWs. Reproduced with permission from Ref. [49], © Wiley-VCH GmbH 2021. (d) Small-angle XRD patterns of the PbBr₂-ligand intermediates (left). The correlation between *d*-spacing of the PbBr₂-ligand intermediates and the morphology of the transformation product from Cs₄PbBr₆ NCs. (e) Schematic illustration of the template-based formation mechanism of CsPbBr₃ NWs or nanocubes. Reproduced with permission from Ref. [75], © American Chemical Society 2021.

nanostructures like NWs to minimize the exposure of high-energy crystal facets [105–107]. Previous reports have demonstrated the transformation of MHP materials from 0D NCs to 1D NWs over time [102]. Kostopoulou et al. observed short, bullet-like MHP NRs from the quenched aliquots in the LARP synthesis, sharing the same growth direction with the longer, ultrathin perovskite NWs finally produced [59]. They attributed the formation and thickening of ultrathin NWs to the oriented attachment mechanism [59]. Specifically, individual ultrathin NRs align and fuse together along anisotropic directions, e.g., $[1\bar{1}0]$ crystal direction, forming longer, single-crystalline ultrathin NWs [59]. Supporting this mechanism, Wang et al. examined the transformation between ultrathin NWs and NRs [49]. They found that ultrathin CsPbBr_3 NWs prepared in cyclohexane became unstable upon dilution, which would decompose and transform into NRs. The resulting NRs possessed higher aspect ratios when the initial NW concentration was higher [49]. They explained this wire-to-rod transformation by the desorption of ligands and extra precursor ions, which stabilized the NWs. This departure of stabilizing agents led to the breakdown of the NW structure post-dilution [49, 108]. The subsequent increases in the length and thickness of produced NRs over time can be explained by the Ostwald ripening mechanism [101]. Interestingly, when the collected precipitates of CsPbBr_3 NRs were redispersed in the supernatant solution, they transformed back into NWs after aging for four days. The resultant NW thickness matched the initial NR diameter (Fig. 5(b)). The authors showed that the NRs that were either too thick or too thin failed to connect with others, supporting their hypothesis that NW formation occurs through end-to-end self-assembly and oriented attachment of NRs (Fig. 5(c)) [49].

3.3 Ligand regulated formation

It is widely recognized that ligands are crucial in directing the morphology of perovskite NCs, as they strongly influence interactions among the precursors and intermediate structures during synthesis [109–112]. Given the limited solubility of PbBr_2 precursor in nonpolar solvents (e.g., hexane and toluene), Chen group hypothesized that the formation of ultrathin NWs can be regulated by ligands that govern the configuration of PbBr_2 -ligand intermediates [75]. To explore this, they applied various ligand combinations to form different PbBr_2 -ligand intermediates in toluene, each displaying a lamellar structure as evidenced by a set of $\{00l\}$ diffraction peaks in their XRD patterns (Fig. 5(d)). They discovered that ligand combinations producing PbBr_2 -ligand intermediates with smaller d -spacings promoted the exclusive formation of ultrathin CsPbBr_3 NWs [75]. They further proposed that these lamellar PbBr_2 -ligand intermediates not only serve as a source of precursor, but also act as an anisotropic template guiding the NW growth. Supporting this hypothesis, they replaced the linear alkyl-amine ligands with a branched trioctylamine ligand, which did not form layered intermediate configurations, and only CsPbBr_3 nanocubes emerged as the sole final product (Fig. 5(e)) [75].

4 Characterizations, properties, and applications of ultrathin MHP NWs

4.1 Morphological and crystal structure determinations

Due to their small diameter, low image contrast, and instability

under electron beam illumination, it could be quite challenging to directly image ultrathin MHP NWs using conventional TEM [113]. To overcome the challenge, Imran et al. in 2016 employed a direct-electron detection camera to replace the conventional charge-coupled device (CCD) camera in their high resolution (HR)-TEM measurements [47]. They found that the ultrathin CsPbBr_3 NWs they synthesized were confined along the $[110]$ crystal direction and elongated along the $[1\bar{1}0]$ direction (Fig. 6(a)). Differently, thicker CsPbBr_3 NWs (thickness of ~ 10 nm) grew along the $[001]$ crystal axis while being constricted along the $[110]$ crystal direction (Fig. 6(a)) [47, 114]. They explained this difference by the inhibited growth along the $[001]$ direction after addition of short chain acids during NW synthesis [25, 114]. Besides TEM, the authors also applied atomic force microscopy (AFM) technique to visualize their ultrathin MHP NWs [47]. By tracing the cross-section profile, Imran et al. found that the ultrathin CsPbBr_3 NWs exhibited a rectangular cross-section, rather than a cylindrical one [47].

In the same year, Zhang et al. used aberration-corrected HR-TEM (AC-HR-TEM) to enhance the image resolution and minimize the beam damage by limiting the applied electron doses [30]. In this way, the spherical aberration, chromatic aberration and astigmatism caused by electric lens can be largely compensated [115, 116]. To prevent the beam damage and achieve atomic-resolution imaging of ultrathin perovskite NWs, Yang group recently applied single-walled carbon nanotubes to confine individual Cs-Pb-I NWs with even single-unit-cell thickness [87]. Since both the graphene substrate and carbon nanotubes can provide NWs from heating, irradiation, and moisture, they were able to use conventional TEM and scanning TEM (STEM) techniques to directly visualize the atomic structure of individual ultrathin NWs without degradation (Fig. 6(b)). Unlike bulkier CsPbI_3 crystals, which commonly exhibit an edge-shared non-perovskite δ -phase structure [117], the atomically thin NW confined in a nanotube displayed a stable corner-shared perovskite phase (Fig. 6(b)). The observed co-existence of α -phase and δ -phase in thicker NWs indicated that geometrical confinement could help stabilize the photoactive α -phase perovskite [87, 118]. However, the lead-iodide octahedral units of these NWs were largely distorted, composed of a contracted cesium framework and an expanded iodine framework (Fig. 6(c)) [87]. Interestingly, they found that the orientation of each octahedral units varied under each STEM scan (Fig. 6(c)), which could result from their intrinsic structure instability and/or NW rotation [119]. To gain further dynamical insights, they applied AC-HR-TEM along with a high-efficiency direct-electron detection camera with a wide range of electron dose rates to achieve atomic resolution and high frame rates, capturing transient structural dynamics *in situ* [87]. This setup allowed them to trace each atom column over time using atom-tracing algorithms, enabling them to reconstruct the dynamic behaviors of MHP NWs at unprecedented resolution.

To determine the crystallographic information of ultrathin MHP NWs, XRD patterns are typically measured and analyzed [49, 59]. These ultrathin MHP NWs exhibit non-uniform diffraction peak broadening due to their anisotropic 1D morphology [120, 121]. For example, in the case of CsPbBr_3 NWs with a cubic phase, the (100) diffraction peak is significantly narrower than other diffraction peaks due to the large crystallite size only along the wire axial $[001]$ direction [63]. Moreover, the diffraction peaks of ultrathin MHP NWs often shift to smaller angles (i.e., larger d -spacings) compared to their standard patterns, signifying substantial lattice expansions

typical absorption peak position of their nanocube or bulk crystal counterparts (> 500 nm) [4, 128]. This strong anisotropic quantum confinement effect may contribute to the high PLQYs of MHP NWs, despite their extensive exposed surfaces and lattice distortion [129]. The highest reported PLQY for ultrathin CsPbBr₃ NWs reached 77%, with a cyan emission peak at 496 nm, accompanied by a shoulder peak at 500 nm, indicating possible impurities or aggregations in the sample [47]. However, as the NW diameter further decreases, the PLQY often drops significantly due to increased surface defects as evidenced by the shortened PL lifetimes, indicating an increase in nonradiative decay processes in thinner NWs [47, 86, 130, 131]. Additionally, optical properties of ultrathin MHP NWs can be tuned by changing the halide composition from Cl to Br to I, resulting in a PL peak shift from ultraviolet to red [30, 56, 60]. This trend is analogous to that observed in MHP perovskite nanocubes [8, 71]. Besides optical property characterizations, in 2020, Stern et al. advanced the study of ultrathin MHP NWs by applying conductive AFM technique to measure the electrical conductivity of individual ultrathin CsPbBr₃ and CsPbBr_xI_{1-x} NWs [132]. They found that for ultrathin CsPbBr₃ NWs, compared to the results gained from mixed-halide NWs, the measured *I*-*V* curves exhibited higher currents and a steeper curve slope, indicating the presence of deeper trap-states after halide mixing. Additionally, the average rise-voltage for pure-bromide NWs was also significantly lower, suggesting more crystalline defects in CsPbBr_xI_{1-x} NWs. Interestingly, the NW conductivity increased after the addition of iodide ions due to its larger atomic diameter and lower electron affinity [132]. Their study provided the first electrical characterizations of single ultrathin NWs and offered insights into the effects of anion exchange within ultrathin MHP NWs.

Building on these unique electrical and optical properties, ultrathin MHP NWs have shown promise in LED applications [38, 133, 134]. Fu et al., for instance, fabricated blue perovskite LEDs (PeLEDs) using ultrathin CsPbBr₃ NW arrays synthesized through an AAO template-based method [86]. The current density-voltage-luminance (*J*-*V*-*L*) curves for the resulting PeLEDs revealed that turn-on voltages increased with enlarging the bandgap of the NWs (Fig. 7(a)), while working current density decreased at the same driving voltage [86]. This phenomenon was attributed to hindered electron tunneling caused by the large Al₂O₃ barrier and lower carrier density in the ultrathin NWs [135, 136]. The maximum luminance achieved by these NW-based PeLEDs reached 96 cd/m² (cyan), 47 cd/m² (sky-blue), 13 cd/m² (blue), operating at 6.5, 6.8, and 7 V, with corresponding external quantum efficiencies (EQEs) of 7.1%, 3.2%, 0.9%, respectively (Fig. 7(b)). The reduced performances in the latter two devices were attributed to increased surface defects caused by a geometry mismatch between circular pores and the cubic phase perovskites of the applied ultrathin NWs [86].

Due to their anisotropic geometry and quantum confinement effects, ultrathin MHP NWs also exhibit unique polarized optical and optoelectronic properties [49, 137, 138]. When excited with linearly polarized light, NW solutions usually display a polarized PL behavior [131, 139–141]. Leveraging this property, Wang et al. fabricated a linearly polarized light detector using ultrathin CsPbBr₃ NWs through a brushing-assembled film method (Fig. 7(c)) [49]. The device showed its highest absorption coefficient and emission ratio when the electric field of the light was aligned parallel to the NW's axial direction (Fig. 7(d)), contrasting with the lowest value when aligned radially [49]. Upon excitation, the photocurrent

Table 1 Summary table of reported synthesis of ultrathin CsPbBr₃ NWs

Crystal phase	Abs. peak (nm)	PL peak (nm)	PL FWHM (nm)	Average PL lifetime (ns)	PLQY (%)	Synthetic method	Application	Average diameter (nm)	Reference(s)
Orthorhombic	484	496	16	4.9	77	Hot injection		5.1 ± 0.5	[47]
Orthorhombic	472	481, 491	18	2.8	40	Hot injection		4.1 ± 0.7	[47]
Orthorhombic	455, 467	473, 483	33	2.5	30	Hot injection		3.4 ± 0.5	[47]
	442	465	26		30	Hot injection		2.2 ± 0.2	[30]
Orthorhombic	445	460				Solvothermal		2.6	[91]
Cubic	420	430			< 1	RT colloidal synthesis		1.5 ± 0.5	[63]
Cubic	444	465			21.13	Post-synthetic heat treatment		3.1 ± 0.6	[63]
Orthorhombic	427	445	23.7			LARP			[59]
Orthorhombic	441	454	22.6			LARP		2.6	[59]
Orthorhombic	454	462	16.2			LARP		6.1	[59]
Orthorhombic	~ 450	475				LARP		~ 3	[56]
	433	447	27		60	Post-synthetic treatment		2.1	[73]
Orthorhombic	413, 448	509			60	LARP		3.8 ± 0.1	[60]
Orthorhombic	413, 448	498			47	LARP		3.8 ± 0.1	[60]
		433, 457				Template-assembled		2	[85]
	426	432	~ 12	7.1	15.2	Post-synthetic treatment		2.5 ± 0.6	[75]
Cubic	~ 450	~ 460				RT colloidal synthesis	Linear polarized light detector	2–3	[49]
Cubic		467		1.4	4	Template-assembled	PeLED	2.9	[86]
Cubic		481		1.967	16	Template-assembled	PeLED	3.5	[86]
Cubic		492		3.34	27	Template-assembled	PeLED	4.3	[86]
Cubic	~ 425	~ 450				LARP	PSCs	2.5 ± 0.5	[147]

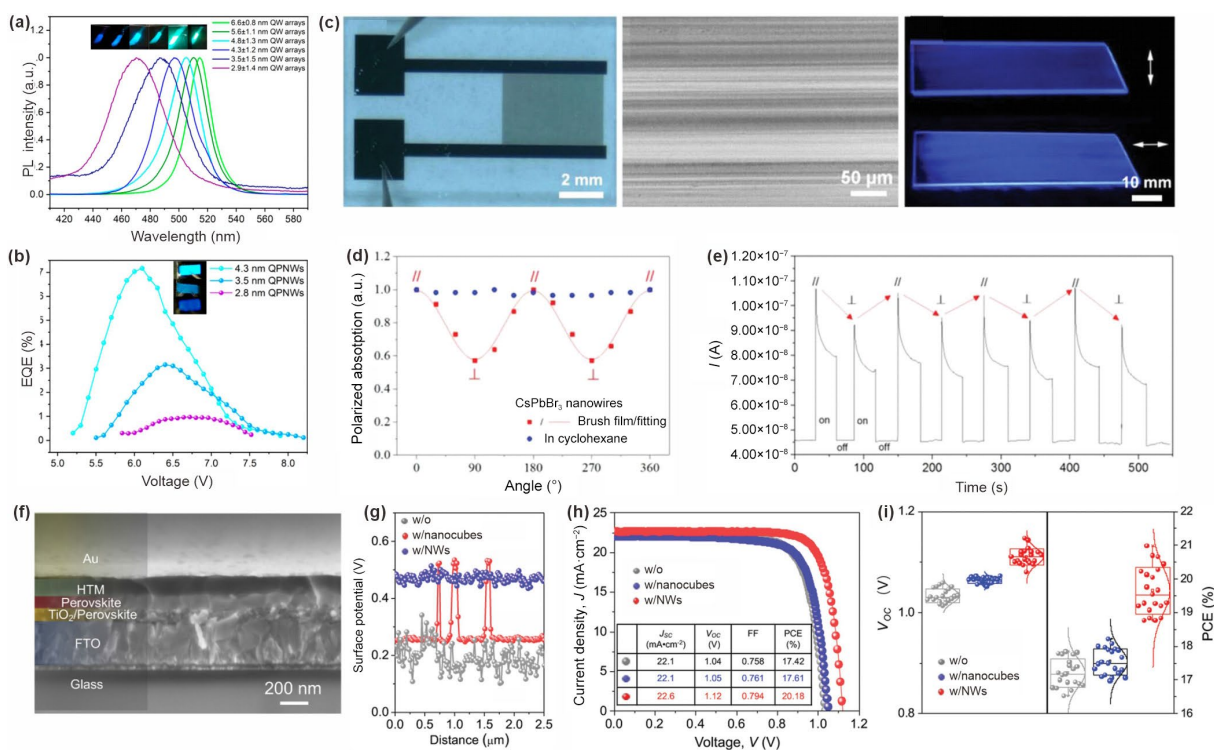


Figure 7 (a) PL spectra of CsPbBr₃ QW arrays with different thicknesses. (b) EQE curves as a function of driving voltage for the QW array based PeLEDs. Reproduced with permission from Ref. [86], © American Chemical Society 2022. (c) The interdigital electrode to measure polarized optoelectronic properties (left). SEM image of the assembled ultrathin CsPbBr₃ NW film prepared by brushing (middle) and corresponding PL image (right). (d) The polarized absorption intensities. (e) The performance of ultrathin CsPbBr₃ NW film-based polarization-sensitive photodetector. Reproduced with permission from Ref. [49], © Wiley-VCH GmbH 2021. (f) Cross-sectional SEM image of the PSC using ultrathin CsPbBr₃ NW incorporated MAPbI₃ thin film. (g) The surface potential variation obtained from kelvin-probe force microscopy (KPFM) surface potential mappings of the MAPbI₃ thin films without NC (w/o), with CsPbBr₃ nanocube, and with ultrathin CsPbBr₃ NW incorporation. (h) *J*-*V* curves (reverse scan) and (i) PCE statistics of the corresponding PSCs. Reproduced with permission from Ref. [147], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2019.

increased instantly, then decreased as charge carriers were captured by trap states in the NWs, eventually stabilized after all these trap states were filled (Fig. 7(e)) [49]. At the “light-off” edge, the photocurrent exhibited a slight increase before dropping back instantly to a stable dark current (Fig. 7(e)), indicating a quick release of the captured charge carriers. This device possessed a response rise time of 0.36 s and a fall time of 0.24 s [49]. While the direction of polarized excitation light only influenced the photocurrent intensity, the response time remained constant. Although the initial photocurrent signal was lower than other polarization-sensitive photodetectors, this method facilitates easy casting of NWs onto various substrates, making it ideal for fabricating flexible optoelectronic devices [49]. Furthermore, integrating these NWs with other hybrid nanomaterials, such as ZnO NWs, silica NWs, and polymers, could potentially enhance sensitivity and broaden the responsive wavelength range of ultrathin MHP NW-based photodetector devices [142–148].

Moreover, the superior optoelectronic properties of MHP materials make them highly promising for solar cell applications [149–151]. For thin-film perovskite solar cells (PSCs), a planar heterojunction typically forms at the interface between the hole-transporting layer (HTL) and the perovskite layer, which can create energy level mismatches that result in considerable energy loss [152–154]. In 2019, Zhang et al. demonstrated the incorporation of ultrathin CsPbBr₃ NWs into a methylammonium lead triiodide (MAPbI₃) perovskite thin-film PSC (Fig. 7(f)) [147]. It was shown

that these incorporated NWs can modify the surface electronic states of the MAPbI₃ perovskite thin film by forming a compositionally graded heterojunction at the perovskite-HTL interface. Furthermore, the ultrathin NWs also acted as a “grating” to enhance light harvesting and energy transfer at the interface. Importantly, the NW morphology was found to be the key parameter to achieve a laterally uniform film surface, as evidenced by surface-potential mappings (Fig. 7(g)). This NW incorporation lead to an increase in the valence band maximum and boosted the device open-circuit voltage (*V*_{OC}) from 1.04 to 1.12 V—a much larger improvement than the 0.01 V increase observed with CsPbBr₃ perovskite nanocube incorporation (Figs. 7(h) and 7(i)) [147]. Consequently, the power conversion efficiency (PCE) of the device increased from 17.42% to 20.18% (Figs. 7(h) and 7(i)), showcasing a promising strategy for further improving PSC performance.

5 Summary and perspectives

In this review, we provide an overview of the advancements in the synthesis, characterization, and properties of ultrathin MHP NWs. Adding to the advantages of MHP materials, the high aspect ratio and anisotropic quantum confinement effects of ultrathin perovskite NWs make this special category of nanomaterials highly promising for both fundamental research and next-generation technological applications. However, such excitement has been held because several critical research areas remain underexplored,

despite the exciting progress made in the field. Here, we outline several critical future directions for advancing ultrathin MHP NWs toward realization of their full potential in diverse applications.

5.1 Controlling NW thickness at the atomic level precision

Achieving precise control over the diameter of ultrathin NWs is crucial, as their optical and electronic properties are highly sensitive to slight variations in size, particularly in the quantum-confined regime. Existing synthesis methods, while effective in producing a wide range of NW sizes, often result in inconsistencies, with discrepancies between NW sizes as observed through TEM images and their corresponding absorption peaks (Table 1). Addressing this challenge requires novel synthesis strategies capable of achieving atomic-level precision in controlling NW diameters and maintaining uniformity across large batches. By refining the synthesis process, researchers can better harness and precisely control the optical and optoelectronic properties in NWs for applications on demand.

5.2 Understanding growth kinetics and formation mechanisms

Despite advancements in ultrathin NW synthesis, the underlying growth mechanisms remain insufficiently understood. Unlike the synthesis of conventional semiconductor NCs with a more covalent bond character, the ionic nature of perovskites leads to their rapid formation, making it difficult to monitor nucleation and growth stages, which are key to controlling their final structure and properties. A clearer understanding of the kinetic processes governing the growth of ultrathin NWs will be critical for achieving consistent results and developing methods for fine-tuning their properties. Such studies can be possibly enabled by *in situ* monitoring tools such as electron microscopy, time-resolved spectroscopy, and X-ray scattering techniques [97, 155–159]. These mechanistic studies should focus on disentangling the factors that influence NW growth, such as temperature, ligand types, precursor composition and concentration, and solvent environment. By better understanding these processes, researchers could unlock more reliable and scalable production of NWs with finely tuned property characteristics.

5.3 Improving stability and environmental resistance

The thermodynamically unfavored morphology of NWs, adding to the intrinsic instability of perovskites, particularly under environmental stressors such as moisture, oxygen, and light, poses a significant barrier to the widespread use of ultrathin NWs in practical applications [48, 49, 160]. Research efforts are needed to focus on developing robust passivation techniques, such as ligand engineering, inorganic encapsulation, or core-shell heterostructure formation, to shield NWs from environmental degradation. In this context, surface modification methods, that have shown promise in enhancing the stability of other types of perovskite nanostructures [161–165], should be adapted and specifically optimized for ultrathin NWs. In addition, novel and more effective passivation strategies should be anticipated upon accumulating knowledge and understandings of the MHP NWs and perovskite materials as general in the field. The goal should be set to achieve ultrathin NWs that maintain their high performance over sufficient periods, making them viable for real-life applications such as solar cells and

displays under desired working environments.

5.4 Expanding compositional space to nontoxic alternatives

The demand for more environmentally friendly materials has pushed researchers to explore alternatives to lead-based perovskites [19, 166–168]. Although lead-halide perovskites offer outstanding optoelectronic properties, their toxicity presents environmental and health concerns. As a result, there is growing interest in lead-free perovskite nanomaterials, including tin-, copper-, bismuth-, and antimony-based systems [23, 24, 81, 169–178]. It is well-known that these lead-free perovskite and perovskite-analogue nanomaterials can offer unique properties, such as tunable bandgaps and band structures, higher stability, along with largely reduced toxicity, making them promising candidates for future applications. Along the line, expanding the family of ultrathin perovskite NWs to include lead-free options should stand as another research focus in the field. This will not only address the lead-induced health and environmental concerns, but also open the door to the creation of new materials, for example, alloyed and/or heterostructure NWs with even wider and more precise tunability in both morphology and properties. These new materials could find applications in diverse fields such as catalysis, sensing, and energy storage, in addition to optoelectronics.

5.5 Exploring unique properties of ultrathin MHP NWs

Ultrathin MHP NWs exhibit distinctive properties that differentiate them from their bulk or thicker counterparts, yet many of these remain underexplored due to their current poor stability. In particular, mechanical properties, such as flexibility, tensile strength and fracture behavior, are critical for applications of NWs in flexible and wearable devices, as well as their integration into mechanical and optoelectronic systems [179–181]. However, these properties of ultrathin MHP NWs have received limited attention to date. Understanding their elasticity index, strength index and plasticity index remains elusive. Bridging this knowledge gap is essential for evaluating the mechanical robustness and deformation behaviors of ultrathin MHP NWs, thereby enabling their practical applications. In addition, the nonlinear optical properties of ultrathin NWs hold significant promise [137, 182–184]. Phenomena such as second-harmonic generation and multiphoton absorption/emission might be enhanced by the quantum confinement effects present in ultrathin geometries [185]. While thicker perovskite NWs have demonstrated nonlinear behaviors, ultrathin MHP NWs are likely to exhibit novel or amplified effects, expanding their potential for photonic devices, optical signal processing, and imaging applications [186, 187]. Moreover, lasing properties of ultrathin MHP NWs remain largely unexplored, with thicker counterparts receiving the primary focus [26, 188]. Ultrathin NWs could potentially enable low-threshold lasing, single-mode emission, or even tunable lasing behaviors owing to their distinct optical and electronic characteristics [189, 190].

In summary, ultrathin MHP NWs represent an exciting frontier in nanomaterial research, offering unique opportunities for a wide range of applications. However, challenges remain in terms of precise synthesis, mechanism understanding, materials' stability, and compositional expanding. Addressing these challenges through innovative and dedicated research will unlock the full potential of ultrathin perovskite NWs, leading to breakthroughs in their

applications in optoelectronics, energy harvesting, catalysis, and beyond. By focusing on these key research directions, it is highly anticipated that researchers can overcome current limitations and drive future innovations in this promising field.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contributions

Y. L. and O. C. proposed the review topic and designed the conceptual framework of the manuscript, Y. L. and Z. Z. performed the literature research and analyzed the relevant data, Y. L. and O. C. drafted and revised the manuscript, Z. L. and Z. Z. participated in the discussion and helped the manuscript revision. O. C. supervised the project.

Use of AI statement

During the preparation of this work, the author, Y. L., used OpenAI's ChatGPT to refine some sentences and enhance the clarity and coherence of the manuscript. After using this tool, the authors thoroughly reviewed and edited the content to ensure accuracy and originality, and take full responsibility for the final version of the publication.

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